

INTERPRETING UNIQUE COLLOIDAL RESPONSE OF TiO<sub>2</sub> NANOMATERIALS TO  
CONTROLLED SONICATION FOR UNDERSTANDING THEIR ASSEMBLY  
CONFIGURATION

by

SIYANG WU

Presented to the Faculty of the Graduate School of  
The University of Texas at Arlington in Partial Fulfillment  
of the Requirements  
for the Degree of

MASTER OF SCIENCE IN ENVIRONMENTAL AND EARTH SCIENCE

THE UNIVERSITY OF TEXAS AT ARLINGTON

DECEMBER 2015

Copyright © by Siyang Wu 2015

All Rights Reserved



### Acknowledgements

I would like to express my sincere and deepest gratitude to my advisor Dr. Hyeok Choi for his great support and guidance. I would also like to thank Dr. Melanie L. Sattler and Dr. Andrew Hunt for being my thesis committee members and for their valuable suggestions and recommendations. I would like to thank the Texas Higher Education Coordinating Board for supporting my research in part through the Norman Hackerman Advanced Research Program (THECB13311). I also appreciate assistances from my lab members, including Wasuu Lawal, Hesam Zamankhan Malayeri, Abolfazl Zakersalehi, and Khuzema Zaveri Burhanuddin. I would like to thank my parents and my twin sister for their support and love through my life.

November 18, 2015

## Abstract

# INTERPRETING UNIQUE COLLOIDAL RESPONSE OF TiO<sub>2</sub> NANOMATERIALS TO CONTROLLED SONICATION FOR UNDERSTANDING THEIR ASSEMBLY CONFIGURATION

Siyang Wu MS

The University of Texas at Arlington, 2015

Supervising Professor: Hyeok Choi

It is important to determine the assembly configuration of engineered nanomaterials (ENMs) particularly between aggregate or agglomerate because the assembly configuration greatly influences their fate and transport behavior in the aquatic environment. Aggregated particles are more subject to segregation upon changes of environmental conditions (vice versa) than agglomerated particles. As a strategic tool for investigating the time-resolved reversible segregating and assembling behavior of ENMs and thus estimating their assembly configuration, controlled sonication process was proposed. It was hypothesized the unique colloidal response of ENMs to sonication, with respect to changes in size, might be their intrinsic property associated with assembly configuration. As a model ENM, three different TiO<sub>2</sub> particles with unique properties (two commercial P-25 and UV 100 and one home-made (HM) TiO<sub>2</sub>) were tested with a programmed sonication process (sonication followed by quiescence, different sonication intensities) under various environmental settings (TiO<sub>2</sub> concentration and pH). When they were dispersed in water, all TiO<sub>2</sub> tested obviously assembled to form much larger particles. Size of P-25 decreased immediately upon sonication and did not change significantly under subsequent quiescence step while sizes of UV 100 and HM gradually decreased and then slowly recovered back to their initial sizes. The trend was generally

observed in all conditions tested. The unique colloidal response of  $\text{TiO}_2$  particles could be explained by their properties associated with assembly configuration. P-25 was concluded to be in aggregate configuration and thus can be practically called nanoparticles while UV 100 and HM were in agglomerate configuration.

## Table of Contents

Acknowledgements .....	iii
Abstract .....	iv
Table of Contents .....	vi
List of Illustrations .....	viii
List of Tables .....	x
Chapter 1 Introduction.....	1
Titanium dioxide (TiO <sub>2</sub> ) .....	2
Research motivation .....	2
Experimental approach.....	3
Chapter 2 Materials and methods .....	5
Chemicals .....	5
Sonication process .....	6
Size measurement and Zeta potential analysis.....	9
Chapter 3 Experimental hypothesis .....	12
Chapter 4 Results and discussion .....	16
Particle assemblage .....	16
Response of TiO <sub>2</sub> particles to sonication.....	17
Response of P-25 to sonication .....	17
Response of UV 100 and HM to sonication .....	17
Discussion on sonication .....	18
Response of TiO <sub>2</sub> particles to quiescence condition .....	19
Effect of sonication intensity .....	20
Effect of sonication intensity on P-25 .....	21
Effect of sonication intensity on UV 100 and HM .....	21

Discussion on sonication intensity.....	23
Effect of TiO <sub>2</sub> concentrations .....	24
Effect of P-25 concentrations .....	24
Effect of UV 100 and HM concentrations .....	25
Discussion on TiO <sub>2</sub> concentration .....	26
Effect of pH conditions.....	27
Zeta potential and pH <sub>PZC</sub> .....	27
Sonication towards different pH adjusted solutions .....	30
Chapter 5 Conclusions.....	32
Chapter 6 Recommendations for future research .....	33
References.....	34
Biographical Information .....	39

## List of Illustrations

Figure 1 P-25, UV 100, and HM.....	6
Figure 2 Probe Sonicator .....	8
Figure 3 pH measurement .....	8
Figure 4 SZ 100 .....	10
Figure 5 An illustration of hydrodynamic size measured by SZ-100 .....	11
Figure 6 An illustration of Zeta potential measured by SZ 100.....	11
Figure 7 Particle assembly configurations: (a) mono-dispersed (completely segregated) primary particles, (b) aggregated particles, and (c) agglomerated particles. ....	14
Figure 8 Relationship between mono-dispersed particles with aggregated particles and agglomerated particles.....	15
Figure 9 Colloidal response of P-25, UV 100, and HM TiO <sub>2</sub> particles to controlled sonication (TiO <sub>2</sub> concentration: 50 mg/l; energy intensity: 60 W; sonication: 15 minutes; quiescence: 15 minutes; pH: 5.2–5.8 with no control).....	19
Figure 10(a) Effect of sonication on P-25 .....	21
Figure 10 (b) Effect of sonication intensity on UV 100.....	22
Figure 10(c) Effect of sonication intensity on HM .....	23
Figure 11(a) Effect of P-25 concentration .....	24
Figure 11(b) Effect of UV 100 concentration.....	25
Figure 11(c) Effect of HM concentration .....	26
Figure 12(a) Effect of solution pH on the size and Zeta potential of P-25.....	28
Figure 12(b) Effect of solution pH on the size and Zeta potential of UV 100.....	29

Figure 12(c) Effect of solution pH on the size and Zeta potential of HM TiO <sub>2</sub> particles .....	29
Figure 13 Colloidal response of P-25, UV 100, and HM TiO <sub>2</sub> particles at different pHs of (a) 3, (b) 5, (c) 7, (d) 9, and (e) 11 to controlled sonication (TiO <sub>2</sub> concentration: 50 mg/l; energy intensity: 60 W; sonication: 15 minutes; quiescence: 15 minutes; pH: 3-11). .....	31

List of Tables

Table 1 The physiochemical properties of TiO<sub>2</sub> Particles ..... 5

## Chapter 1

### Introduction

Nanoscaled materials are materials that have at least one dimension between 1-100 nm. It can be released from either point or nonpoint source, such as manufacturing, landfills, wastewater effluent, storm-water runoff, wet deposition, etc. People can be easily exposed to nanomaterials as they breathe air, drink water and eat food (Wiesner et al. 2006). Engineered nanomaterials (ENMs) are any nanomaterials intentionally and deliberately created for special functions and engineering purposes by human (Kreyling et al. 2010). Since engineered nanomaterials (ENMs) are stronger, lighter, and more reactive, they have been utilized in energy production, medical sector, food products, and many other new applications (Serrano et al. 2009; Boisseau and Loubaton 2011; Weiss et al. 2006). In particular, metal and metal oxide nanoparticles (NPs) are widely studied in the remediation of contaminated water and soil (Mueller and Nowack 2010). Environmental remediation employing NPs is considered as a sustainable and cost-effective cleanup process (Shan et al. 2009). With the increasing usage of NPs in commercial products and environmental remediation areas, concern about their potential environmental risk has been also raised (Wiesner et al. 2006; Brandi et al. 2009; Hammond et al. 2013). Due to the small size, nanoparticles can easily penetrate physiological barriers and cause damage. Researches have shown that some nanoparticles can penetrate skin, enter body, rapidly migrate to organs, and potentially cause serious problems (Buzea et al. 2007). People who are exposed to ENM might have health risk of pulmonary inflammation, genotoxicity, carcinogenicity, and circulatory effect (Savolainen et al. 2010). The toxicity of nanoparticles depends on size, aggregation, composition, etc. Free nanoparticles, which are different from nanostructured thin films or other fixed nanometer-scale objects, they can easily enter the

environment and may cause serious health risk to human. Nanostructured or fixed nanometer-scaled objects have less or no potential health risk if they are well treated (Buzea et al. 2007). Since not all NPs released to the environment are available for exposure of human and living organisms to them, it is important to understand their colloidal behavior under various conditions, which controls their fate and transport in the environment (Praetorius et al. 2012; Sygouni and Chrysikopoulos 2015).

#### Titanium dioxide (TiO<sub>2</sub>)

As one of the most important and widely used ENMs, titanium dioxide (TiO<sub>2</sub>) has been studied as photocatalysts and pigments (Zakersalehi et al. 2013). TiO<sub>2</sub> particles are insoluble in water and they assemble together naturally to form larger clusters like other ENMs. As a result, overall size of TiO<sub>2</sub> particles is much larger than their crystal size and thus they tend to precipitate quickly and filter out easily more than what is extrapolated based on their primary particle size (Keller et al. 2010). The reactivity, mobility, availability of TiO<sub>2</sub> particles can change significantly due to their assembling in aqueous media (Klaine et al. 2008; Domingos et al. 2009). This implies the assembly configuration of TiO<sub>2</sub> particles should be always considered when their fate and transport is assessed. Environmental conditions that affect particle assembling include mainly pH, ionic species and strength, and natural organic matter (French et al. 2009; Xiang et al. 2013).

#### Research motivation

Many studies have been conducted to understand the stability and mobility of TiO<sub>2</sub> particles under various conditions and in natural water resources (Zhang et al. 2008; Battin et al. 2009; Kammer et al. 2010; Gottschalk et al. 2009; Keller et al. 2010; Brunelli et al. 2013). However, there have been no systematic studies to understand the

assembly configuration of TiO<sub>2</sub> particles (i.e., how TiO<sub>2</sub> particles make assemblages), not to mention other ENMs. In particular, it is important to determine whether particles are in aggregate configuration or agglomerate configuration. Aggregated particles are more subject to segregation upon changes of environmental conditions (vice versa) than agglomerated particles. Results by Virkutyte et al. (2014) showed that TiO<sub>2</sub> particles with various assembly configurations exhibited their unique mobility through porous media. As a result, there is a need of an experimental approach to investigate the segregating and assembling behavior of TiO<sub>2</sub> particles and thus to estimate their assembly configuration.

#### Experimental approach

In this study, we propose to use sonication process. Assembled particles, particularly in aggregate configuration, are believed to be easily agitated by sonication and thus transform to small segregated particles. Depending on sonication energy applied to TiO<sub>2</sub> particles, size of even agglomerated particles might decrease upon sonication. We hypothesize the unique colloidal response of TiO<sub>2</sub> particles to controlled sonication, with respect to changes in particle size, might be their intrinsic property associated with their assembly configuration. In order to prove the hypothesis, this study focuses on investigating the time-resolved reversible segregating and assembling behavior of TiO<sub>2</sub> particles under programmed sonication. Three different TiO<sub>2</sub> particles with unique properties (two commercial and one home-made TiO<sub>2</sub>) were tested with a programmed sonication process (sonication followed by quiescence, sonication intensity) under different environmental settings (TiO<sub>2</sub> concentration and pH).

Understanding the unique reversible segregating and assembling behavior of TiO<sub>2</sub> particles and thus their assembly configuration would be beneficial to interpreting their mobility, availability, and treatability in natural environmental systems as well as

water and wastewater treatment facilities that work based on size-dependent exclusion and settling mechanisms.

## Chapter 2

### Materials and methods

#### Chemicals

Three types of TiO<sub>2</sub> ENMs were tested in this study: P-25 (Degussa), UV 100 (Hombikat), and home-made (HM) TiO<sub>2</sub> (Figure 1). P-25 purchased from Evonik Degussa GmbH, Germany shows primary crystal size of 28.2 nm, specific surface area of 53.8 m<sup>2</sup>/g, and mixture of 70% anatase and 30% rutile. P-25 is synthesized by flame hydrolysis. UV 100 purchased from Sachtleben Chhemie GmbH, Germany shows primary crystal size of 5.50 nm, specific surface area of 292 m<sup>2</sup>/g, and 100% anatase crystal phase. UV 100 is synthesized by sulfate process. HM synthesized by sol-gel process in our laboratory has surface area of 231 m<sup>2</sup>/g and amorphous phase. The crystal size, crystal phase, and surface area of three TiO<sub>2</sub> particles were referenced from Virkutyte et al. (2014), where the crystal size of solid phase TiO<sub>2</sub> was measured using XRD based on Scherrer equation and the surface area was measured by N<sub>2</sub> adsorption isotherm. Other chemicals used include hydrogen chloride (HCl) and sodium hydroxide (NaOH) purchased from Sigma-Aldrich, US.

Table 1 The physiochemical properties of TiO<sub>2</sub> Particles

Name	Crystal size (nm)	Crystal phase	Surface area (m <sup>2</sup> /g)	Synthesis
P-25	28.2	A:R=7:3	53.8	Flame hydrolysis
UV 100	5.5	A	292	Sulfate process
HM	-	Amorphous	231	Sol-gel process

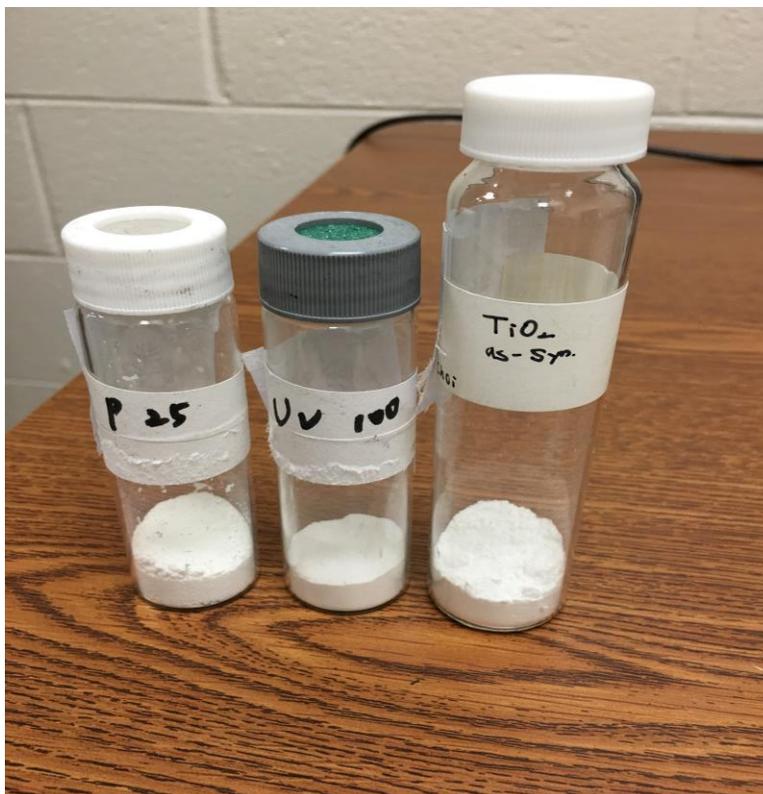


Figure 1 P-25, UV 100, and HM

#### Sonication process

Each of  $\text{TiO}_2$  ENMs (P-25, UV 100, and HM) was dispersed in water at a fixed concentration of 50 mg/l to briefly investigate their response to sonication and thus to determine their assembly configuration (either aggregate or agglomerate). Sonication process was applied to the suspension to investigate how particles uniquely segregate and assemble as a function of sonication time followed by quiescence time. A sonicator (Misonix Sonicator S-4000) (Figure 2) with capability to accurately manipulate the total energy delivered to particle suspension was utilized. To prevent  $\text{TiO}_2$  suspension from

overheating during sonication, suspension was cooled down in a cold-water bath. Based on preliminary studies, sonication was programmed at probe energy intensity of 60 W and sonication for 15 minutes followed by quiescence for 15 minutes (standard condition), where  $\text{TiO}_2$  particles showed well-developed segregating and assembling behavior (Taurozzi et al. 2011).

The effect of concentration of  $\text{TiO}_2$  particles in a range of 20–200 mg/L on their response to sonication was also investigated. The experiment was conducted without pH control and thus pH was naturally maintained at 5.4 for P-25, 5.2 for UV 100, and 5.8 for HM. Meanwhile, the experiment above under the standard condition was resumed under controlled pH conditions in a range of 3–11 adjusted by adding HCl or NaOH in order to examine the effect of pH on the response of  $\text{TiO}_2$  particles to sonication. A pH meter is shown in Figure 3. For the examination, variation of the Zeta potential and hydrodynamic size of  $\text{TiO}_2$  particles was monitored and their point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was also determined. Lastly, in order to investigate the effect of sonication energy, different probe sonication intensities were tested in a range of 30–100 W under the standard condition except for sonication time. Instead of 15 minutes, 10 minutes for sonication and 10 minutes for quiescence were applied because high intensities caused severe erosion of the sonication probe tip (Mandzy et al. 2005).



Figure 2 Probe Sonicator



Figure 3 pH measurement

### Size measurement and Zeta potential analysis

The hydrodynamic size and Zeta potential (i.e., electric potential at shear layer) of TiO<sub>2</sub> particles in suspension were monitored upon their segregation and assembling in response to sonication under different pH conditions. A particle size and Zeta potential analyzer (SZ-100, Horiba, Japan) (Figure 4) utilizing dynamic light scattering (DLS) and laser Doppler electrophoresis (LDE), respectively, was applied.

DLS is widely used and effective for measuring size of particles when they are dispersed in suspension (Pecora 2000). Based on light scattering of particles, their hydrodynamic diameter is calculated by using the Stoke-Einstein equation (referenced from the technical section of SZ-100).

Particle size was measured at the 173° detection angle for 2 minutes. Particle size was measured every 5 minutes during the sonication and quiescence process.

Equation Stokes-Einstein

$$d = kT/3\pi\eta D$$

d: particle diameter

D: dispersion coefficient

k: Boltzmann constant

$\eta$ : Dispersion medium viscosity

T: Absolute temperature

. LDE measures the frequency of the scattered light and determines the velocity and mobility of particles. Zeta potential is calculated from mobility by using the Smoluchowski model (referenced from the technical section of SZ-100).

Average particle size and Zeta potential were determined from more than three measurements.

Equation Smoluchowski

$$\zeta = \frac{U\eta}{\varepsilon * f(Ka)}$$

$\zeta$ : Zeta Potential

U: Electrical mobility

$\varepsilon$ : Solvent dielectric constant

$\eta$ : Solvent viscosity

f(Ka): Henry coefficient

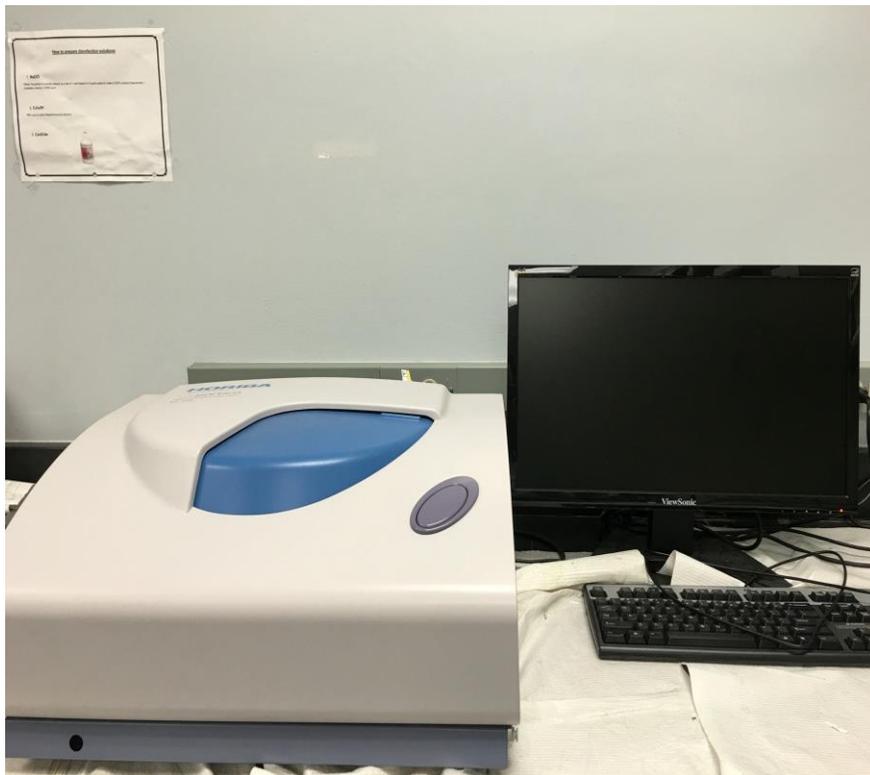


Figure 4 SZ 100

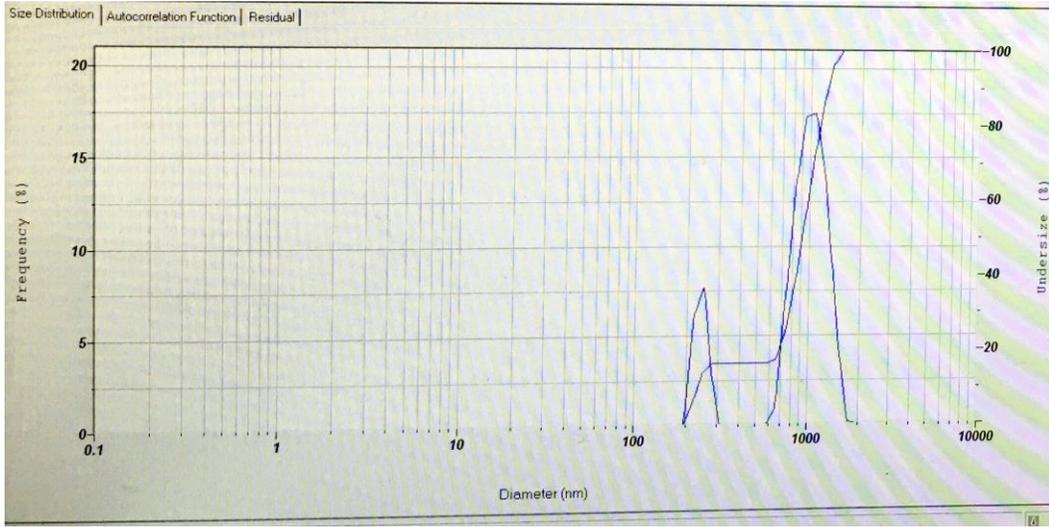


Figure 5 An illustration of hydrodynamic size measured by SZ-100

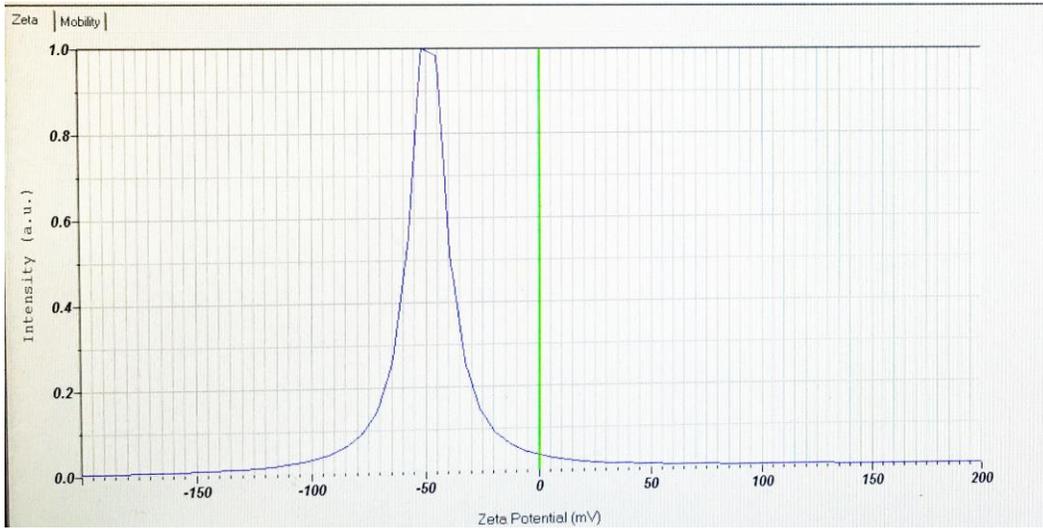


Figure 6 An illustration of Zeta potential measured by SZ 100

## Chapter 3

### Experimental hypothesis

Particle assembly configuration is important because assembly configuration itself often has more influence on the fate and transport behavior of particles in the environment than their primary size. As shown in Figure 7, particles at nanoscale are assumed to be present in either mono-dispersed (i.e., completely segregated) configuration, aggregated configuration, or agglomerated configuration. Aggregate can be defined as assemblage of particles that are loosely and physically attached at their corners and edges while agglomerate can be defined as assemblage of particles that are rigidly bound at their faces. From the definitions, configurations in Figure 7 (a) and Figure 7 (b) might be easily interchangeable upon physical and chemical interactions between primary particles. Meanwhile, segregate configuration in Figure 7(a) transforms to agglomerate configuration Figure 7 (c) by fusion, sintering, and/or crystal growth during synthesis of primary particles, and thus transformation of agglomerate configuration in Figure 7 (c) back to segregate configuration in Figure 7(a) occurs less likely. Aggregated particles are subject to segregation upon change of environmental conditions (vice versa) and thus they might be more mobile and available, compared to agglomerated particles.

Sonication breaks particles in suspension via either erosion or fracturing. Erosion is effective to break weak bonds between particles in aggregate configuration while fracturing attacks weak structures in agglomerated particles such as imperfections and cracks (Mandzy et al. 2005; Taurozzi et al. 2011). Sonication energy, once optimized, is believed to be strong enough to agitate particles mostly by mechanically segregating aggregated particles (i.e., from Figure 7(b) to Figure 7(a)) but not enough to break down agglomerated particles (i.e., from Figure 7(c) to Figure 7(a)). The relationship is shown in Figure 8. Depending on sonication energy applied to TiO<sub>2</sub> particles, size of even

agglomerated particles might decrease upon sonication. We hypothesize the unique colloidal response of TiO<sub>2</sub> particles to controlled sonication, with respect to changes in particle size, might be their intrinsic property associated with their assembly configuration. Based on the configurations shown in Figure 7, nanoscale particles in aggregate configuration might be more sensitive to sonication and more mobile in the environment and thus they can be practically called NPs in comparison to nanoscale particles in agglomerate configuration which can be called nanostructured particles (NSPs) (Virkyte et al. 2014).

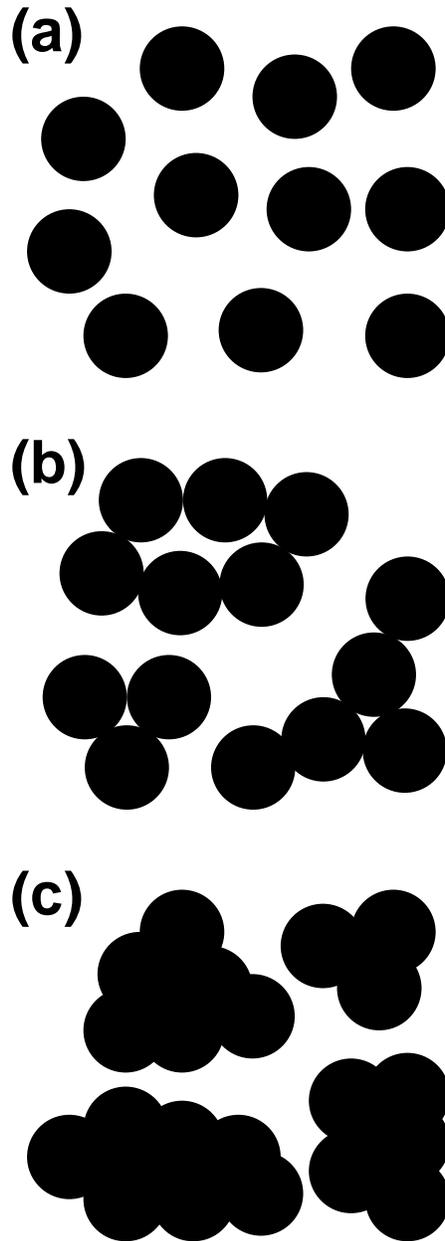


Figure 7 Particle assembly configurations: (a) mono-dispersed (completely segregated) primary particles, (b) aggregated particles, and (c) agglomerated particles.

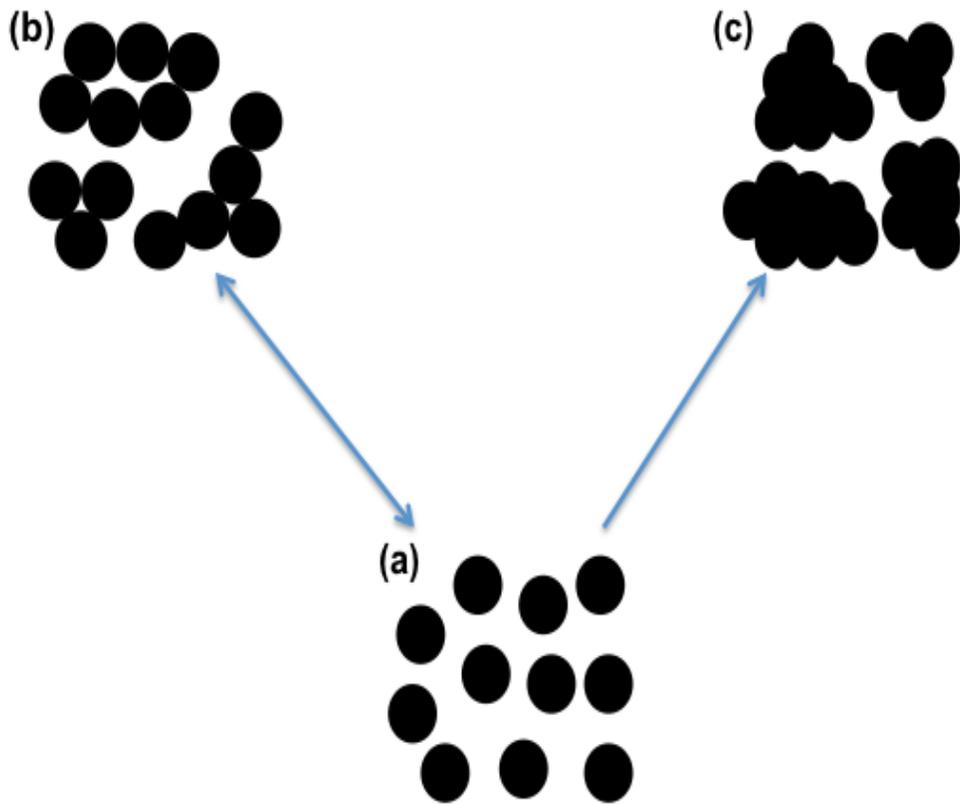


Figure 8 Relationship between mono-dispersed particles with aggregated particles and agglomerated particles.

## Chapter 4

### Results and discussion

In order to prove the hypothesis, the time-resolved reversible segregating and assembling behavior of TiO<sub>2</sub> particles under programmed sonication was investigated. TiO<sub>2</sub> particles under natural conditions start either assembling to make large assemblages or segregating to make small assemblages when they are dispersed in water. As shown in Figure 9, P-25 showed the smallest size at around 653 nm before sonication; UV 100 showed size at around 3854 nm; and HM showed the largest size at around 6284 nm. Considering sizes of primary crystal particles are at 28.2 nm for P-25 and 5.50 nm for UV 100, TiO<sub>2</sub> particles obviously assembled to form much larger particles.

### Particle assemblage

Van der Waals forces exist in all molecules and particles in liquid. Identical materials have the strong potential to attract each other and to repulse dissimilar materials in liquid. Nanoparticles have strong van der Waals forces and thus they assemble together when they disperse in liquid (Min et al 2008). Particle-particle interactions have significant roles in controlling the particle assemblage, which is described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability. According to the DLVO theory, the assemblage of nanoparticles in an aqueous environment is ascribed to the attractive Van der Waals (VDW) force as well as the repulsive electrical double-layer (EDL) interaction (Petosa et al 2010). Since particles at nanoscale have the high surface to volume ratio, they highly assemble (Saltiel et al. 20004). Three types of TiO<sub>2</sub> particles tested in this study (P-25, UV 100, and HM) assembled well to form much larger clusters than their

primary crystal sizes. P-25 and UV 100 have the crystal size of 28.2 nm and 5.5 nm and they assembled to 653 nm and 3854 nm in water, respectively.

#### Response of TiO<sub>2</sub> particles to sonication

Since TiO<sub>2</sub> particles are synthesized by different processes, they might exhibit inherently different assembly configurations and thus unique segregation behavior in response to sonication (Taurozzi et al. 2011).

##### *Response of P-25 to sonication*

Size of P-25 decreased from 653 nm to around 210 nm immediately within 5 minutes of sonication and the size did not further decrease significantly. The similar result for P-25 was also observed by Jiang et al. (2009), reporting size of P-25 decreased to 180 nm after 5 minutes of sonication and then became fixed. Taurozzi et al. (2011) pointed out that size of particles is stabilized after they break down to a specific size.

##### *Response of UV 100 and HM to sonication*

The response of UV 100 and HM to sonication was different from that of P-25. Their sizes kept decreasing over 15 minutes of sonication. Size of UV 100 almost continuously decreased from 3854 nm to 1675 nm while size of HM also continuously decreased from 6284 nm to 1797 nm. The result investigated under the specific sonic intensity implies that bindings between particles for UV 100 and HM might be stronger than particles for P-25. Sonication increases collision frequency of particles and enhances particle-particle interactions, resulting in particle segregation (so-called peaking behavior) (Taurozzi et al. 2011).

### *Discussion on sonication*

P-25 presumably in aggregate configuration segregated immediately and easily upon application of sonication energy while UV 100 and HM presumably in agglomerate configuration continued to disassemble over sonication time. Size of P-25 at 133 nm after 15 minutes of sonication is relatively close to its primary crystal size of 28.2 nm. This implies that several primary P-25 particles formed a small assemblage and most of them were effectively segregated upon sonication. The observation that P-25 particles were not completely broken to its primary particles might be explained by many factors associated with their synthesis method, storage state, sonication intensity, and erosion mechanism (Zhang et al. 2008; Ding and Pacek 2008; Teleki et al. 2008). Meanwhile, size of UV 100 at 1675 nm after sonication is still much larger than its primary crystal size of 5.50 nm. This implies UV 100 is considered to be in agglomerate configuration although UV 100 successfully disassembled by both segregation and fracturing mechanisms during sonication (the same for HM).

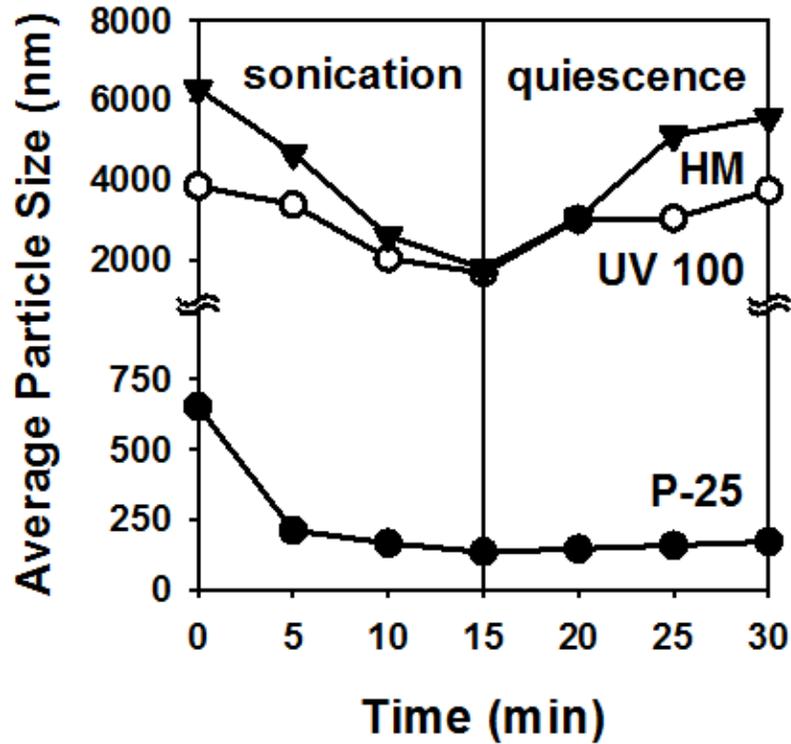


Figure 9 Colloidal response of P-25, UV 100, and HM TiO<sub>2</sub> particles to controlled sonication (TiO<sub>2</sub> concentration: 50 mg/l; energy intensity: 60 W; sonication: 15 minutes; quiescence: 15 minutes; pH: 5.2–5.8 with no control).

#### Response of TiO<sub>2</sub> particles to quiescence condition

After sonication, TiO<sub>2</sub> suspension stayed under quiescence condition to investigate how TiO<sub>2</sub> particles re-assemble over time back to their initial size, as shown in 9. Size of P-25 did not change significantly during the quiescence step. Size at around 133–170 nm was maintained, indicating no significant re-assembling. Taurozzi et al. (2011) and Horst et al.

(2012) explained that size of particles could decrease only to size of their primary aggregates which are larger than their primary particles and those primary aggregates are hard to re-assemble. The result for UV 100 and HM is interesting. Their sizes under quiescence condition increased almost back to their initial sizes before sonication. There was a continuous re-assembling process for UV 100 and HM. Those particles seemed unstable after sonication compared to stable P-25. The sonication intensity applied to this specific test might have physically and/or chemically altered the surface characteristics of TiO<sub>2</sub> particles differently. Supercritical condition could be created by sonication, inducing locally high temperature and pressure enough to produce hydroxyl radicals along with strong mechanical shocking forces. Those conditions would change the hydrophilicity and stability of TiO<sub>2</sub> particles differently (Taurozzi et al. 2011; Horst et al. 2012).

#### Effect of sonication intensity

The reversible segregating and assembling behavior of TiO<sub>2</sub> particles might vary upon sonication intensity. In order to confirm whether the trends observed in Figure 9 are specific to the sonication intensity used for the study or not, the effect of sonication intensity on changes in size of TiO<sub>2</sub> particles was investigated, as shown in Figure 10. Similar trends to those shown in Figure 9 were observed under different sonication intensities at 30, 40, 60, and 100 W. TiO<sub>2</sub> concentration was at 50 mg/l; energy intensity was at 30-100 W; sonication and quiescence time was at each of 10 minutes; pH was at around 5.2–5.8 with no pH control. Sonication time was at 10 minutes in this specific study instead of 15 minutes because combination of 15 minutes and 100 W greatly damaged the sonication probe.

*Effect of sonication intensity on P-25*

Size of P-25 decreased steeply upon sonication and stayed at the same upon quiescence condition (Figure 10 (a)). For example, at the 30 W, particle size decreased from 653 nm to 273 nm after 5 minutes of sonication, and the size was around 217 nm after 10 minutes of sonication. Meanwhile, after 10 minutes of quiescence, the sizes did not increase significant; the size was around 243 nm.

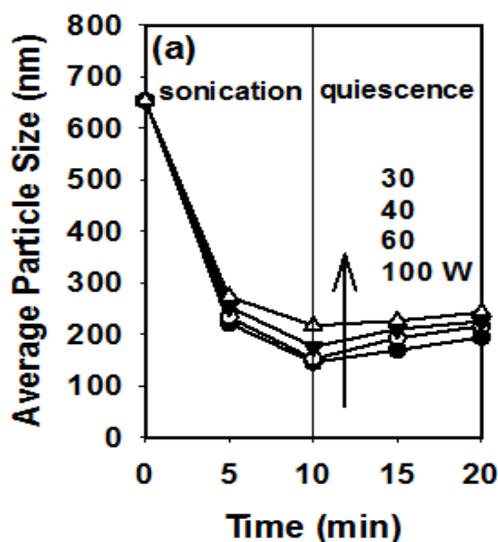


Figure 10(a) Effect of sonication on P-25

*Effect of sonication intensity on UV 100 and HM*

Sizes of UV 100 and HM decreased gradually and recovered slowly back to their initial sizes (Figure 10 (b) and 10 (c)). At 30 W, the size of UV 100 decreased from 3854 nm to 3654 nm after 5 minutes of sonication (5.2% of size decreases); the size was around 3502 nm after 10 minutes of sonication, which indicated that the sonication was not strong enough to break particle bonds. Even at 100 W of sonication, the size of UV 100 decreased to 2261 (41% of size decreases) and 1721 nm (55% of size decreases) after 5

and 10 minutes of sonication, respectively. The size after 100 W of sonication was smaller than the size after 30 W of sonication, but it was still much larger than the primary crystal size (5.5 nm). HM TiO<sub>2</sub> particle was shown the same behavior of UV 100. At 30 W, the size of HM decreased from 6284 nm to 5368 nm after 5 minutes of sonication (14.6% of size decreases) and was around 3500 nm after 10 minutes of sonication (44% of size decreases); at the 100 W, the size of HM was around 4805 nm (23.5% of size decreases) and 2013 nm (68% of size decreases) after 5 and 10 minutes of sonication, respectively.

During the quiescence processes, the sizes of UV 100 and HM TiO<sub>2</sub> particles gradually recovered back at all sonication intensities. The sizes of UV 100 were around 2039-3593 nm after 5 minutes of quiescence and were around 3431-4485 nm after 10 minutes of quiescence. The sizes of HM TiO<sub>2</sub> particles were around 3182-4588 nm after 5 minutes of quiescence and were around 4522-5166 nm after 10 minutes of quiescence as the sonication intensity ranging from 30-100 W.

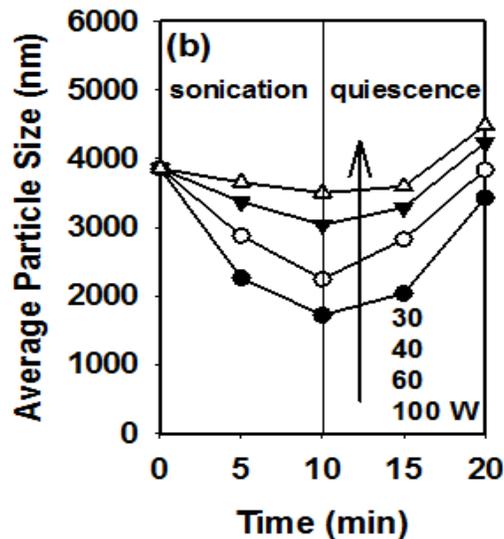


Figure 11 (b) Effect of sonication intensity on UV 100

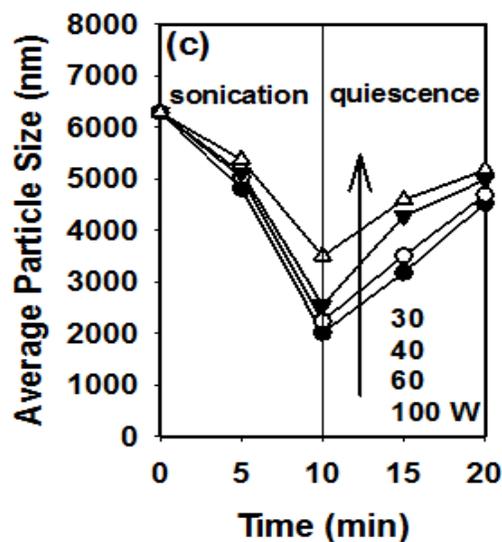


Figure 12(c) Effect of sonication intensity on HM

*Discussion on sonication intensity*

As expected, higher intensities induced more breaking of particles, resulting in smaller sizes after sonication. Small particles made under high sonication intensities ended up with small particles under quiescence condition. Interestingly, degree of the effect of sonication intensity on changes in particle size was different. The intensities investigated in this specific study, ranging 30–100 W, were not able to make any significant difference in the unique colloidal behavior of P-25. However, the intensities significantly impacted UV 100. High intensity at 100 W greatly changed size of UV 100 from 3854 nm to 1721 nm while low intensity at 30 W did not change it significantly. From the results, it can be speculated that P-25 is in aggregate configuration and thus more sensitive to sonication even at low intensities while UV 100 is in agglomerate configuration and thus less sensitive, requiring high sonication intensities for particle segregation.

### Effect of TiO<sub>2</sub> concentrations

In order to confirm whether the trends observed in Figure 9 and 10 are specific to the concentration used for the studies or not, different concentrations of TiO<sub>2</sub> particles at 20, 50, 100, and 200 mg/l were examined.

### Effect of P-25 concentrations

As shown in Figure 11 (a), size of P-25 in all concentrations decreased immediately upon sonication. Particle size decreased from 348 to 100 nm, 546 to 123 nm, 653 to 133 nm, and 707 to 181 nm after 15 minutes of sonication as the concentration was 200, 100, 50, 20 mg/l, respectively. While, during the quiescence process, the sizes recovered less than 50 nm in all concentrations, which was consistent with the behaviors shown above, and proved that P-25 was very sensitive to sonication in all concentrations.

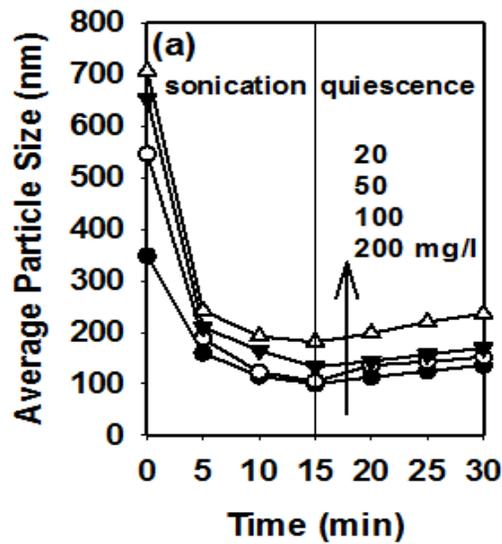


Figure 13(a) Effect of P-25 concentration

*Effect of UV 100 and HM concentrations*

Meanwhile, sizes of UV 100 and HM in all concentrations decreased gradually upon sonication and recovered slowly under quiescence condition, as shown in 11 (b) and 11 (c). For example, the initial size of UV 100 in DI water at 200 mg/l of concentration was around 2285 nm. The size decreased to 660 nm after 15 minutes of sonication, and recovered back to 1886 nm after 15 minutes of quiescence. Also at the same condition, the size of HM TiO<sub>2</sub> particle decreased from 1960 nm to 732 nm and recovered back to 2224 nm after the quiescence.

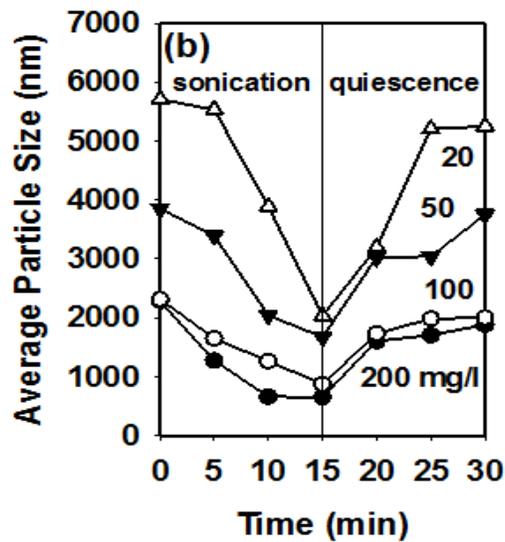


Figure 14(b) Effect of UV 100 concentration

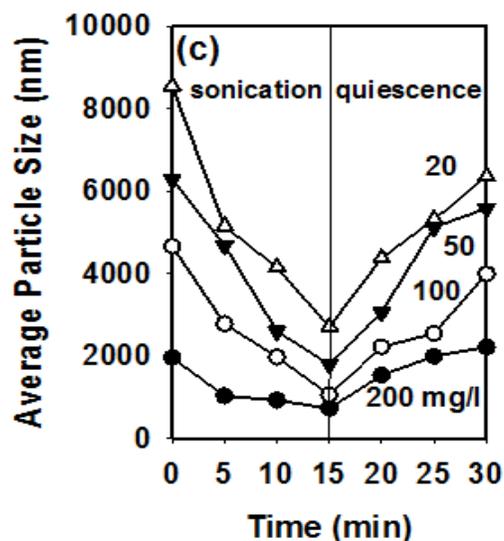


Figure 15(c) Effect of HM concentration

*Discussion on TiO<sub>2</sub> concentration*

As shown in Figure 11 (a), (b), and (c), higher concentrations of TiO<sub>2</sub> particles generally induced smaller particles from the beginning. When mass concentration increased from 20 to 200 mg/l, particle size decreased from 707 to 348 nm for P-25, 5708 to 2285 nm for UV 100, and 8540 to 1960 nm for HM. This phenomenon was also observed in previous studies. Suttioponparnit et al. (2011) proved that increase in concentration results in decreased pH and thus increased Zeta potential which inhibits particles from assembling. In addition, higher concentrations require less energy per unit mass for segregation (Ding and Pacek 2008). The sonication conditions were same as the first experiment, that is, 15 minutes of sonication, 15 minutes of quiescence, and sonication at 60 W. While, the Y-axis scale for three particles are different.

As expected, low concentrations of TiO<sub>2</sub> particles seemed more sensitive to sonication, resulting in more significant changes in their size. The previously observed trends in the segregating and assembling behavior of TiO<sub>2</sub> were applicable to a wide range of TiO<sub>2</sub> concentrations.

### Effect of pH conditions

#### *Zeta potential and pH<sub>PZC</sub>*

In order to confirm whether the trends observed in Figure 9-11 are specific to the natural pH used for the studies or not and to investigate effect of pH on the colloidal response of TiO<sub>2</sub> to sonication, different pH conditions at 3, 5, 7, 9, and 11 were examined. First, particle size and Zeta potential were measured over pH conditions, as shown in Figure 12 (a), (b), and (c). Mandzy et al. (2005) pointed out that particles with Zeta potential between -30 mV and + 30 mV are unstable and subject to assembling due to van der Waals force. TiO<sub>2</sub> at acidic conditions has positive Zeta potential due to adsorption of H<sup>+</sup> onto the surface of TiO<sub>2</sub> (Lee et al. 2010). Point of zero charge of TiO<sub>2</sub> (pH<sub>PZC</sub>) was determined to be at around 5.5 for P-25, 3.8 for UV 100, and 3.0 for HM. Small crystal UV 100 (5.50 nm) showed lower pH<sub>PZC</sub> at 3.8 than large crystal P-25 (28.2 nm) with pH<sub>PZC</sub> of 5.5, which was explained by Dunphy Guzman et al. (2006) and Lee et al. (2010). Based on the results shown in Figure 12 (a), (b), and (c), size of TiO<sub>2</sub> particles was generally correlated with Zeta potential over pHs. At around the pH<sub>PZC</sub> of TiO<sub>2</sub> particles, they showed the largest size due to particle attraction (i.e., negligible repulsion force between particles). At pHs larger than 9, Zeta potential did not further increase (rather decreased) and thus size did not decrease (rather increased) in all TiO<sub>2</sub> solutions. Addition of NaOH to control such high pHs is known to cause high ionic strength and compressed electric

double layer, resulting in decreased particle repulsion (Jiang et al. 2009; Suttiponparnit et al. 2011; Horst et al. 2012).

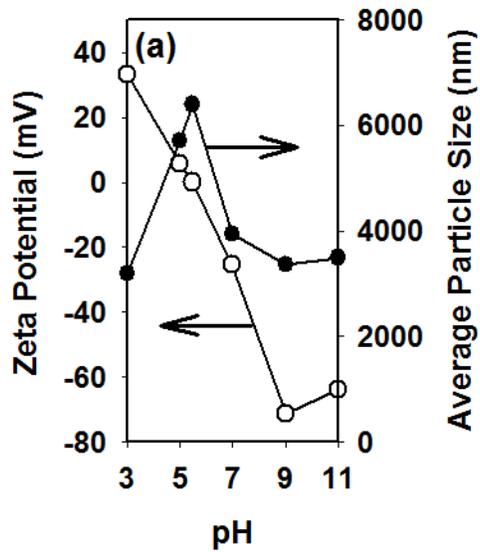


Figure 16 Effect of solution pH on the size and Zeta potential of P-25

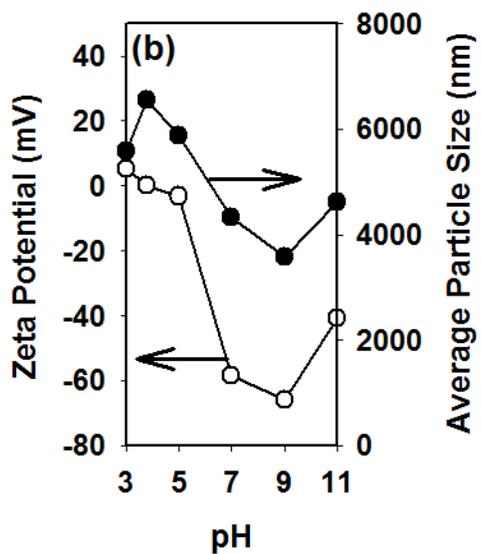


Figure 17 Effect of solution pH on the size and Zeta potential of UV 100

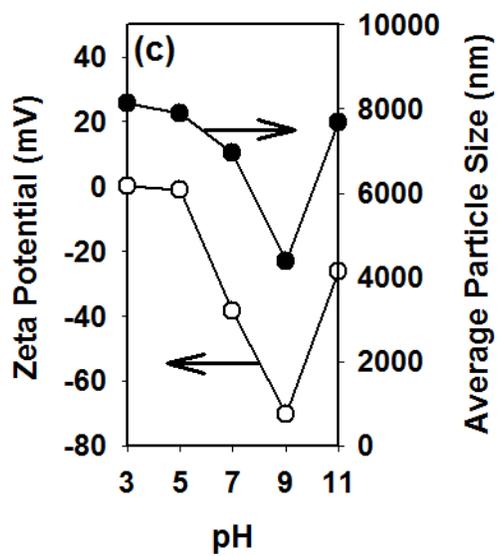


Figure 18 Effect of solution pH on the size and Zeta potential of HM TiO<sub>2</sub> particles

#### *Sonication towards different pH adjusted solutions*

In comparison to size of P-25 at 653 nm under the natural condition (Figure 9), P-25 in the pH-controlled solutions showed much larger size at 2985–6402 nm. In general, large size particles were formed in all pH-controlled TiO<sub>2</sub> solutions and thus settled out in a short time. Figure 13 shows the colloidal behavior of TiO<sub>2</sub> under sonication and quiescence condition at different pHs. The behaviors were very similar to the general trends observed in Figure 9-11. Particles at pHs of 3, 5, and 11 showed greater changes in their size. TiO<sub>2</sub> particles were more sensitive to sonication when their initial sizes were larger. Assembling rate of UV 100 in the pH-controlled solutions was much slower than that in the natural solution, and thus the assembling rate of UV 100 was as slow (or negligible) as that of P-25.

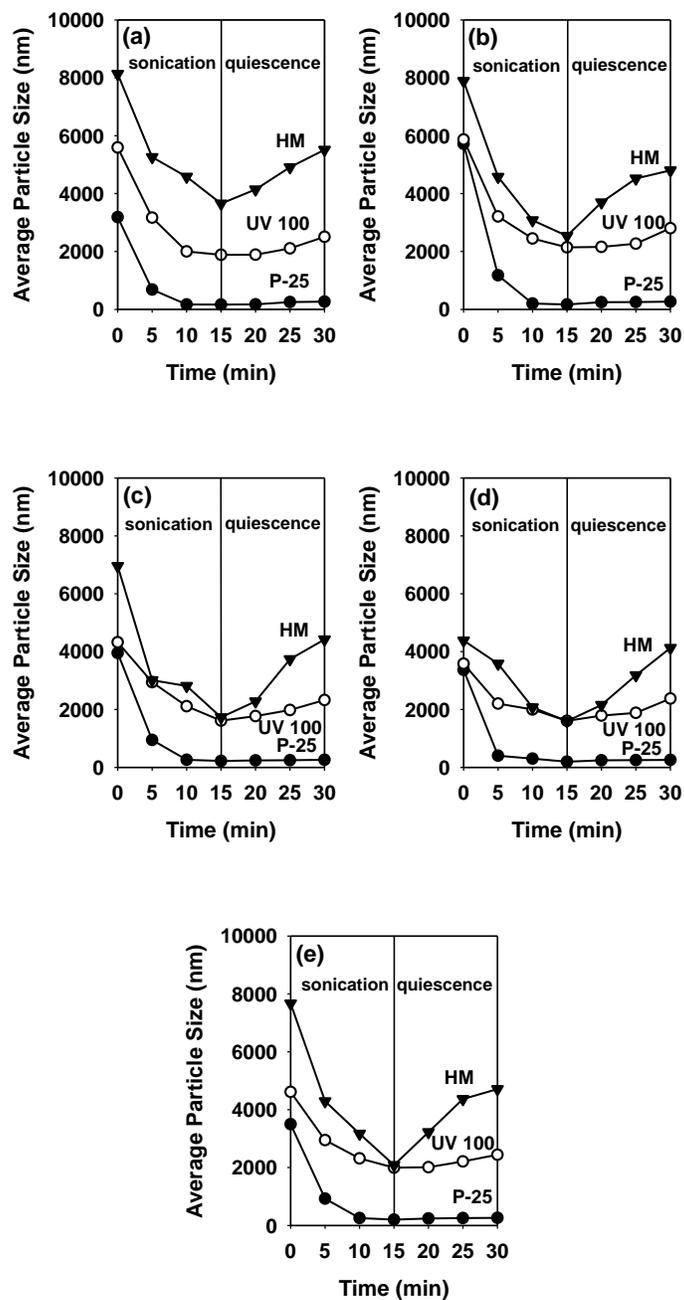


Figure 19 Colloidal response of P-25, UV 100, and HM TiO<sub>2</sub> particles at different pHs of (a) 3, (b) 5, (c) 7, (d) 9, and (e) 11 to controlled sonication (TiO<sub>2</sub> concentration: 50 mg/l; energy intensity: 60 W; sonication: 15 minutes; quiescence: 15 minutes; pH: 3-11).

## Chapter 5

### Conclusions

The time-resolved reversible segregating and assembling behavior of  $\text{TiO}_2$  particles under controlled sonication program was investigated to estimate their assembly configuration. When they were dispersed in water, all  $\text{TiO}_2$  tested obviously assembled to form much larger particles. Size of P-25 decreased immediately upon sonication and did not change significantly under subsequent quiescence condition, while sizes of UV 100 and HM decreased gradually and then recovered slowly back to their initial sizes. The trends were generally observed in all cases under different sonic intensities, solution pHs, and  $\text{TiO}_2$  concentrations. The unique colloidal response of  $\text{TiO}_2$  particles to sonication could be explained by their properties associated with assembly configuration. P-25 was concluded to be in aggregate configuration and thus it can be practically called NPs, while UV 100 and HM were in agglomerate configuration and thus they can be called NSPs. Since  $\text{TiO}_2$  is selected just as a model ENM for the concept demonstration, the hypothesis and the experimental approach are widely applicable to many other ENMs assembled in various media to better understand and predict their colloidal behavior.

## Chapter 6

### Recommendations for future research

Ionic strength and ionic species are two important factors that have strong influences on the size and mobility of nanomaterials. In this study, all the experiments to investigate the response of  $\text{TiO}_2$  to sonication were done without controlling ionic strength and species. In order to better understand their responses to sonication in the natural water systems, studies on the effect of ionic strength and ionic species should be conducted. In addition, stabilizing agents have the potential to adsorb to  $\text{TiO}_2$  surface and stabilize  $\text{TiO}_2$  particles in aqueous media. A test should be conducted accordingly to investigate changes in the size of  $\text{TiO}_2$  particles encapsulated with such stabilizing agents in nature. In order to further verify whether the approach employing controlled sonication is valid to identify particle assembly configuration between aggregation and agglomeration, the experiments should be revisited with more commercially available  $\text{TiO}_2$  particles. Eventually, we should be able to categorize all commercial  $\text{TiO}_2$  nanomaterials into practical nanoparticles, nanostructured particles, or bulk particles.

## References

- Battin TJ, Kammer Fvd, Weilharter A, Ottofuelling S, Hofmann T (2009) Nanostructured TiO<sub>2</sub>: transport behavior and effects on aquatic microbial communities under environmental conditions. *Environ Sci Technol* 43:8093-8104.
- Boisseau P, Loubaton B (2011) Nanomedicine, nanotechnology in medicine. *C R Phys* 12:620-636.
- Brandi G, Nobili E, Girolamo SD, Grazi G, Fiorentino M, Golfieri R, Biasco G (2009) Nanotechnology-related environment, health, and safety research. *Environ Health Persp* 117:433-434.
- Brunelli A, Pojana G, Callegaro S, Marcomini A (2013) Agglomeration and sedimentation of titanium dioxide nanoparticles (*n*-TiO<sub>2</sub>) in synthetic and real waters. *J Nanopart Res* 15:1684-1694.
- Buzea C, Pacheco II, Robbie K (2007) Nanomaterials and nanoparticles: source and toxicity. *Biointerphases* 2: MR 17-MR 71.
- Ding P, Pacek AW (2008) De-agglomeration of goethite nano-particles using ultrasonic comminution device. *Powder Technol* 187:1-10.
- Domingos RF, Tufenkji N, Wilkinson KJ (2009) Aggregation of titanium dioxide nanoparticles: role of a fulvic acid. *Environ Sci Technol* 43:1282-1286.
- Dunphy Guzman KA, Finnegan MP, Banfield JF (2006) Influence of surface potential on aggregation and transport of titania nano-particles. *Environ Sci Technol* 40:7688-7693.
- French RA, Jacobson AR, Kim B, Isley SL, Penn RL, Baveye PC (2009) Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles. *Environ Sci Technol* 43:1354-1359.

- Gottschalk F, Sonderer T, Scholz RW, Nowack B (2009) Modeled environmental concentrations of engineered nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT, Fullerenes) for different regions. *Environ Sci Technol* 43:9216-9222.
- Hammond SA, Carew AC, Helbing CC (2013) Evaluation of the effects of titanium dioxide nanoparticles on cultured *Rana catesbeiana* tailfin tissue. *Front Genet* 4:251.
- Horst AM, Ji ZX, Holden PA (2012) Nanoparticle dispersion in environmentally relevant culture media: a TiO<sub>2</sub> case study and considerations for a general approach. *J Nanopart Res* 14:1014.
- Jiang JK, Oberdörster G, Biswas P (2009) Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11: 77-89.
- Kammer Fvd, Ottofuelling S, Hofmann T (2010) Assessment of the physico-chemical behavior of titanium dioxide nanoparticles in aquatic environments using multi-dimensional parameter testing. *Environ Pollut* 158:3472-3481.
- Keller AA, Wang HT, Zhou DX, Lenihan HS, Cherr G, Cardinale BJ, Miller R, Ji ZX (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environ Sci Technol* 44: 1962-1967.
- Klaine SJ, Alvarez PJJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR (2008) Nanomaterials in the environment: behavior, fate, bioavailability, and effects. *Environ Toxicol Chem* 27:1825-1851.
- Kreyling WG, Semmler-Behnke M, Chaudhry Q (2010) A complementary definition of nanomaterial. *Nano today* 5:165-168.
- Lee MK, Uhm YR, Rhee CK, Lee YB (2010) Organic suspension behavior of rutile TiO<sub>2</sub> nanoparticles with high specific surface area. *Mater Trans* 51:2157-2161.

- Mandzy N, Grulke E, Druffel T (2005) Breakage of TiO<sub>2</sub> agglomerates in electrostatically stabilized aqueous dispersions. *Powder Technol* 160:121-126.
- Min YJ, Akbulut M, Kristiansen K, Golan Y, Israeachvili J (2008) The role of interparticle and external forces in nanoparticle assembly. *Nat Mater* 7:527-538.
- Mueller NC, Nowack B (2010) Nanoparticles for remediation: solving big problems with little particles. *Elements* 6:395-400.
- Pecora R (2000) Dynamic light scattering measurement of nanometer particles in liquids. *J Nanopart Res* 2:123-131.
- Petosa AR, Jaisi DP, Quevedo IR, Elimelech M, Tufenkji N (2010) Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions. *Environ Sci Technol* 44:6532-6549.
- Praetorius A, Scheringer M, Hungerbühler K (2012) Development of environmental fate models for engineered nanoparticles—a case study of TiO<sub>2</sub> nanoparticles in the Rhine River. *Environ Sci Technol* 46:6705-6713.
- Saltiel C, Chen Q, Manickavasagam S, Schadler LS, Siegel RW, Menguc MP (2004) Identification of the dispersion behavior of surface treated nanoscale powders. *J Nanopart Res* 6: 35-46.
- Savolainen K, Pylkkanen L, Norppa H, Falck G, Lindberg H, Tuomi T, Vippola M, Alenius H, Hameri K, Koivistro J, Brouwer D, Mark D, Bard D, Berges M, Jankowska E, Posniak M, Farmer P, Singh R, Kromback F, Bihari P, Kasper G, Seipenbusch M (2010) Nanotechnologies, engineered nanomaterials and occupational health and safety-A review. *Safety Sci* 48:957-963.
- Serrano E, Rus G, García-Martínez J (2009) Nanotechnology for sustainable energy. *Renew Sust Energ Rev* 13: 2373-2384.

- Shan G, Yan S, Tyagi R, Surampalli R, Zhang T (2009) Applications of nanomaterials in environmental science and engineering: review. *Pract. Period. Hazard. Toxic Radioact. Waste Manage* 13: 110-119.
- Suttiponparnit K, Jiang JK, Sahu M, Suvachittanont S, Charinpanitkul T, Biswas P (2011) Role of surface area, primary particle size, and crystal phase on titanium dioxide nanoparticle dispersion properties. *Nanoscale Res Lett* 6:27.
- Sygouni V, Chrysikopoulos CV (2015) Characterization of TiO<sub>2</sub> nanoparticle suspensions in aqueous solutions and TiO<sub>2</sub> nanoparticle retention in water-saturated columns packed with glass beads. *Chem Eng J* 262:823-30.
- Taurozzi JS, Hackley VA, Wiesner MR (2011) Ultrasonic dispersion of nanoparticles for environmental, health and safety assessment—issues and recommendations. *Nanotoxicology* 5:711-729.
- Teleki A, Wengeler R, Wengeler L, Nirschl H, Pratsinis SE (2008) Distinguishing between aggregates and agglomerates of flame-made TiO<sub>2</sub> by high-pressure dispersion. *Powder Technol* 181:292-300.
- Weiss J, Takhistov P, McClements DJ (2006) Functional materials in food nanotechnology. *J Food Sci* 71:R107– R116.
- Wiesner MR, Lowry GV, Alvarez P, Dionysiou D, Biswas P (2006) Assessing the risks of manufactured nanomaterials. *Environ Sci Technol* 40(14):4336-4345.
- Virkutyte J, Al-Abed SR, Choi H, Bennett-Stamper C (2014) Distinct structural behavior and transport of TiO<sub>2</sub> nano- and nanostructured particles in sand. *Colloid Surface A* 443 (2014): 188-94.
- Xiang CC, Yang F, Li M, Jaridi M, Wu NQ (2013) Experimental and statistical analysis of surface charge, aggregation and adsorption behaviors of surface-functionalized titanium dioxide nanoparticles in aquatic system. *J Nanopart Res* 15:1293-1304.

- Zakersalehi A, Nadagouda M, Choi H (2013) Suppressing NOM access to controlled porous TiO<sub>2</sub> particles enhances the decomposition of target water contaminants. Catal Comm 41:79-82.
- Zhang Y, Chen YS, Westerhoff P, Hristovski K, Crittenden JC (2008) Stability of commercial metal oxide nanoparticles in water. Water Res 42:2204-2212.

### Biographical Information

Siyang Wu earned her bachelor degree in Coastal and Environmental Science at the Louisiana State University (LSU) at 2013. She started her master degree in Environmental and Earth Science Program at the University of Texas at Arlington in 2014. During her master academic study, she worked as a graduate research assistant in Dr. Hyeok Choi's lab in Civil and Environmental Engineering Department. She is interested in environmental remediation, air/water pollution control, and environmental management. She did her MS research on "interpreting unique colloidal response of TiO<sub>2</sub> nanomaterials to controlled sonication for understanding their assembly configuration".